

ON THE ELECTRONIC SPECTRA OF 2-BROMO-AND 3-BROMOPYRIDINE IN DIFFERENT STATES AND IN SOLUTIONS

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ABSTRACT. The ultraviolet absorption spectra of 2-bromo- and 3-bromopyridine in all the three phases and also of their solutions have been investigated and a tentative assignment of the bands of the vapours has been made

In the vapour phase, 3-bromopyridine exhibits two systems of discrete bands, one due to the $n \rightarrow \pi^*$ transition (Transition I) and the other due to $\pi \rightarrow \pi^*$ transition (Transition II). In the liquid state, in the solid state at -180°C and in solution in alcohol, the $n \rightarrow \pi^*$ transition is absent and only one system of bands due to $\pi \rightarrow \pi^*$ transition is observed. In the spectrum due to the solution in 3-methyl pentane, however, the $n \rightarrow \pi^*$ transition persists. It is suggested that the molecules of 3-bromopyridine form associated groups through the nitrogen sp^2 electron and the hydrogen atom of neighbouring molecules in the states of aggregation of the pure substance.

In the case of 2-bromopyridine it is confirmed that the $n \rightarrow \pi^*$ transition is absent not only in the state of aggregation and in solution in alcohol but also in its spectra due to the vapour phase and solution in 3-methyl pentane probably due to the intramolecular inductive influence of the bromine atom on the sp^2 electron of the adjacent nitrogen atom as suggested by earlier workers.

INTRODUCTION

It is now an established fact (Kasha 1950, Rush and Spomer, 1952) that in the near ultraviolet absorption spectrum of *N*-heterocyclic compounds in the vapour state there is a second system of bands due to the excitation of a nonbonding sp^2 electron of the nitrogen atom to the first unfilled π -molecular orbital of the ring called $n \rightarrow \pi^*$ transition besides the system due to $\pi \rightarrow \pi^*$ transition

Recently, Banerjee (1956, 1957) studied the absorption spectra of pyridine and the three isomeric picolines in the liquid state and in the solid state at low temperature and observed that the second system of bands due to the $n \rightarrow \pi^*$ transition disappears with liquefaction of the vapour and it is absent also in the spectrum due to the substances in the solid state. The absence of the $n \rightarrow \pi^*$ transition in the liquid and solid states was explained by him on the assumption that in these states of aggregation the molecules are associated through weak

virtual bonds formed by the non-bonding electron of the nitrogen atom and the hydrogen atom of neighbouring molecules

Roy (1958) studied the absorption spectra of solutions of pyridine in different solvents and obtained both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in solutions in cyclohexane, 3-methyl pentane and carbon tetrachloride. But in the spectrum due to the solution in isobutyl alcohol, the $n \rightarrow \pi^*$ transition was found to be absent and this was attributed to the formation of a bond between the pyridine molecule and the OH group of alcohol molecule through the non-bonding electron of the nitrogen atom.

Stephenson (1954) studied the absorption spectra of some substituted pyridine compounds including 2-bromopyridine and 3-bromopyridine dissolved in iso-octane and ethyl alcohol. In the case of solution of 3-bromopyridine in ethyl alcohol the $n \rightarrow \pi^*$ transition was found to be absent, but it appeared in the spectrum due to the solution in iso-octane. In the case of 2-bromopyridine, however, no change in intensity was observed in the low energy region when the solvent was changed from iso-octane to alcohol. The $n \rightarrow \pi^*$ transition was found to be absent also in the spectrum due to vapour of this substance. He concluded from these results that the $n \rightarrow \pi^*$ transition was absent in the spectrum due to 2-bromopyridine. He explained this absence of the $n \rightarrow \pi^*$ transition on the assumption that inductive attraction of halogen atom attached to the adjacent carbon atom increases the binding energy of the nonbonding electrons of the nitrogen atom and consequently the bands due to the $n \rightarrow \pi^*$ transition are shifted to the region of the bands due to $\pi \rightarrow \pi^*$ transition.

The present work was undertaken to investigate the ultraviolet absorption spectra of 2-bromo- and 3-bromopyridine in the vapour state and to analyse the bands, if possible, because Stephenson (1954) had not analysed these bands. It was also intended to find out whether the $n \rightarrow \pi^*$ transition is actually absent in the case of 2-bromopyridine in the vapour state.

The absorption spectra of these compounds in the solid and liquid states and in solutions in different solvents have also been studied in order to compare these spectra with those due to the substances in the vapour state.

EXPERIMENTAL

Chemically pure samples of 2-bromo- and 3-bromopyridine supplied by Fluka, Switzerland, were fractionated and the proper fractions were distilled under reduced pressure before use. To study the spectra due to the vapour absorption, cells of length 50 cm and 10 cm were used. The cell was filled up with the vapour at saturation vapour pressure at different temperatures and the spectra due to the vapour at different densities were photographed. Two separate electrical heaters, one for the absorption cell and the other for the bulb containing the liquid and

attached to the absorption cell, were used to control the temperature. The reservoir containing the liquid was always kept at a temperature about 5°C lower than that at any part of the absorption cell. To produce a low pressure in the vapour in the absorption tube, the tube was kept at the room temperature while the bulb containing the liquid was immersed in a suitable low temperature bath.

To record the bands due to $\pi \rightarrow \pi^*$ transition in 3-bromopyridine, the 10 cm cell was used and it was kept at the room temperature while the reservoir was kept at 0°C. The 50-cm cell under similar conditions was used to record the bands due to the $n \rightarrow \pi^*$ transition. In the case of 2-bromopyridine an absorption cell of length 50 cm was used and the reservoir was kept at 0°C for studying the $\pi \rightarrow \pi^*$ transition and at 50°C for studying $n \rightarrow \pi^*$ transition.

Very thin films of thickness of the order of a few microns of the substances in the liquid and solid states were required to produce absorption bands due to $\pi \rightarrow \pi^*$ transition. Thicker films of the liquids were also used to find out whether bands corresponding to $n \rightarrow \pi^*$ transition were present.

The solvents used to study the absorption spectra of the substances in the solutions were ethyl alcohol and 3-methyl pentane. The solvents were found to produce no absorption band in the region under consideration. In this case, a brass cell 5mm thick provided with quartz windows was used and the strength of the solution was varied from .01% to 08% by weight. Spectrograms were taken on Agfa Isopan film with a Hilger E J spectrograph giving a dispersion of the order of 3Å per mm in the region of 2600Å. Iron arc spectrum was taken on each spectrogram as a comparison.

Microphotometric records were taken with a Kipp and Zonen self-recording microphotometer. The absorption spectra were calibrated with the help of microphotometric records of the iron lines using the method described in an earlier paper (Sirkar and Misra, 1959).

As the Raman and infrared spectra of these two substances had not been studied by previous workers, infrared absorption spectra of very thin films of the substances were recorded with a Perkin-Elmer Model 21 spectrophotometer using rock salt optics in order to find out the ground state vibrations and these were used to verify the excited state frequencies derived from the ultraviolet absorption spectra.

RESULTS AND DISCUSSION

Microphotometric records of the absorption spectra of 3-bromo- and 2-bromopyridine in different states and in solutions are reproduced in Figs. 1-6. The wave numbers of the bands in cm^{-1} , approximate intensities and their probable assignments are given in Tables I, II, III and IV.

3-Bromopyridine

(a) *Spectrum of the vapour phase.*

The absorption spectrum of 3-bromopyridine in the vapour phase (Fig. 1) shows two distinct systems of bands under different conditions of pressure and length of absorbing column of the vapour. With the vapour at the saturation pressure at 4°C and with an absorption tube 50 cm long, a system of absorption bands starting at about 35000 cm^{-1} followed by region of complete absorption is observed. The bands of this system are sharp and narrow and following Kasha (1950), they have been attributed to the $n \rightarrow \pi^*$ transition (Transition I). At lower pressure of the vapour in a shorter cell, the second band system appears in the region 36000 cm^{-1} to 39000 cm^{-1} and the broad bands of this system resemble those due to other substituted benzenes arising from the $\pi \rightarrow \pi^*$ transition (Transition II). The analysis of the bands of these two systems is discussed separately in the following sections

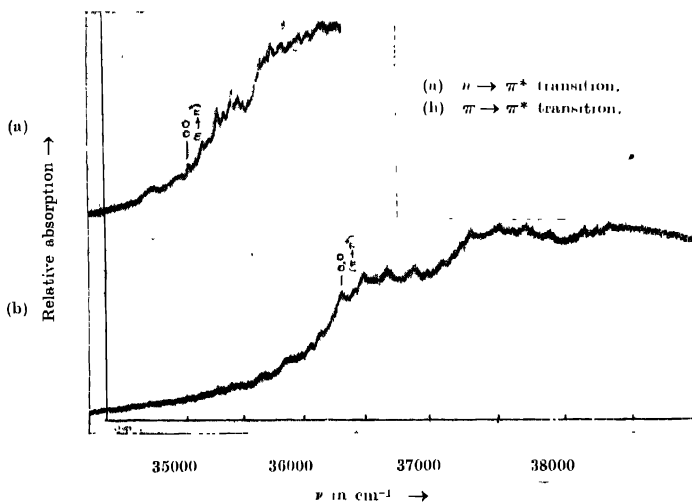


Fig. 1. Microphotometric records of the ultraviolet absorption spectra of 3-bromopyridine in the vapour state.

i) $\pi \rightarrow \pi^*$ transition (Transition II)

The strong band at 36300 cm^{-1} in this system has been taken as the 0, 0 band. Most of the remaining strong bands represent transitions involving excited state

TABLE I
Ultraviolet absorption bands of 3-bromopyridine in the vapour phase

Wave no. (cm ⁻¹) and intensity	Assignment	Wave No. (cm ⁻¹) and intensity	Assignment
Transition I ($n \rightarrow \pi^*$)		Transition II ($\pi \rightarrow \pi^*$)	
34778 (wb, diffuse)	?	35866 (mw)	0 - 434
34925 (wb, diffuse)	'		
35080 (w)	0, 0	35986 (w)	0 - 314
35183 (s)	0 + 103	36064 (mw)	0 - 236
35238 (w)	0 + 158	36123 (w)	0 - 177
35310 (s)	0 + 230	36300 (s)	0, 0
35359 (s)	0 + 279	36458 (s)	0 + 158
35412 (w)	0 + 103 + 230	36526 (w)	0 + 226
35429 (s)	0 + 349	36579 (w)	0 + 279
35469 (s)	0 + 158 + 230	36672 (s)	0 + 372
35517 (ms)	0 + 2 + 103 + 230	36835 (w)	0 + 158 + 372
35564 (ms)	0 + 2 + 103 + 279	36875 (s)	0 + 575
35621 (w)	0 + 2 + 158 + 230	36971 (w)	0 + 671
35659 (m)	0 + 579	37081 (m)	0 + 781
35702 (w)	0 + 158 + 2 + 230	37163 (m)	0 + 863
35752 (m)	0 + 2 + 103 + 2 + 230	37246 (m)	0 + 946
35867 (s, b)	0 + 2 + 158 + 2 + 230 ($\pi \rightarrow \pi^*$)	37309 (s)	0 + 1009
35986 (ms, b)	0 + 2 + 279 + 349 ($\pi \rightarrow \pi^*$)	37532 (s)	0 + 372 + 863
36062 (ms, b)	0 + 2 + 349 + 279 ($\pi \rightarrow \pi^*$)	37721 (s)	0 + 1421
		37884 (s)	0 + 375 + 1009
		38171 (s)	0 + 863 + 1009
		38247 (m)	0 + 946 + 1009
		38324 (m)	0 + 2 + 1009

vibrational frequencies 158, 226, 279, 372, 575, 671, 781, 863, 946, 1009 and 1421 cm⁻¹ and also ground state frequencies 177, 236, 314 and 430 cm⁻¹ as shown in Table I. In order to find out the ground state vibrational frequencies, the infrared absorption spectrum of a very thin film of 3-bromopyridine with NaCl optics was studied. The wave numbers of the observed infrared bands are 695(s),

785(s), 870(vw), 1002(s), 1082(s), 1090(h)*, 1188(vw), 1319(vw), 1416(s), 1462(ms), 1558(h) and 1572(ms). The strength of the absorption at the bands are given in parentheses.

The infrared absorption bands at 695 cm^{-1} , 785 cm^{-1} , 870 cm^{-1} , 1002 cm^{-1} and 1082 cm^{-1} may be the ground state frequencies corresponding to the excited state frequencies 671 cm^{-1} , 781 cm^{-1} , 863 cm^{-1} , 946 cm^{-1} and 1009 cm^{-1} respectively. The absorption band apparently arising from the excited state frequency 1421 cm^{-1} may have actually been produced by two excited state vibrations, the corresponding ground state frequencies being 1416 cm^{-1} and 1462 cm^{-1} observed in the infrared and thus may explain why this band is broader than the other bands.

The ground state values of the excited state frequencies 158 cm^{-1} , 226 cm^{-1} , 279 cm^{-1} and 372 cm^{-1} may probably be 177 cm^{-1} , 236 cm^{-1} , 314 cm^{-1} and 430 cm^{-1} respectively observed on the longer wavelength side of the 0, 0 band as $v \rightarrow 0$ transitions.

(ii) $n \rightarrow \pi^*$ transition (Transition I)

The $n \rightarrow \pi^*$ transition of 3-bromopyridine lies in the region 35000 cm^{-1} to 36000 cm^{-1} . Assuming the band at 35080 cm^{-1} as the 0, 0 band of this system, the other bands can be assigned as progression of frequencies 103, 158, 230, 279, 349 and 579 cm^{-1} and their combinations as shown in Table I. The bands at 35857 cm^{-1} , 35986 cm^{-1} and 36062 cm^{-1} are not narrow line-like bands unlike the other bands of this system. The high intensity and large breadth of these bands may be due to superposition of bands due to $n \rightarrow \pi^*$ on the bands of the $\pi \rightarrow \pi^*$ transition. Thus the band at 35857 cm^{-1} may be assigned as an $n \rightarrow \pi^*$ transition ($0 + 2 \times 158 + 2 \times 230$) superimposed on the (0-434) band of the $\pi \rightarrow \pi^*$ transition. Similarly, the other two bands are formed by superposition of the bands ($0 + 2 \times 279 + 349$) and ($0 + 2 \times 349 + 279$) of $n \rightarrow \pi^*$ system on the bands (0-314) and (0-236) of the $\pi \rightarrow \pi^*$ system respectively.

No attempt has been made to assign the two broad diffuse bands at 34778 cm^{-1} and 34925 cm^{-1} since they have structures entirely different from those of bands due to both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.

(b) Spectra of the solutions

In the spectrum of .01% solution of 3-bromopyridine in ethyl alcohol (Fig. 2) only three broad bands are observed in the region 36000 cm^{-1} to 38000 cm^{-1} , the 0,0 band being assumed to be at 36197 cm^{-1} . The other two bands form progression of excited state frequency 966 cm^{-1} and its harmonics. The nature and position of these bands suggest that they belong to the $\pi \rightarrow \pi^*$ system. With increased concentration, the long wavelength side was photographed, but no

* 'h' indicates a hump in the absorption curve.

band system corresponding to the $n \rightarrow \pi^*$ transition observed in the vapour could be detected.

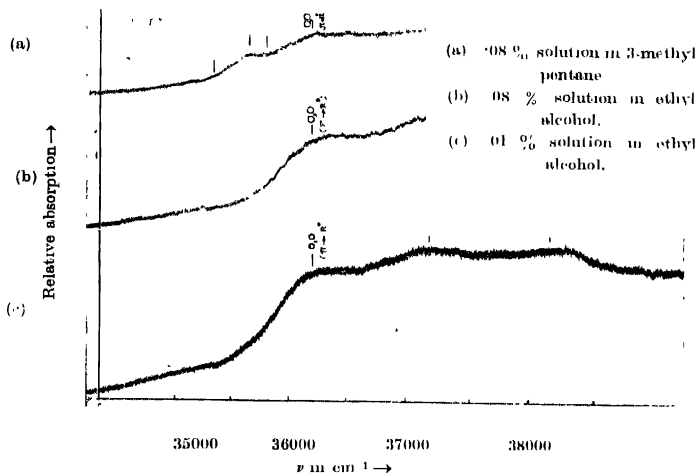


Fig. 2. Microphotometric records of the ultraviolet absorption spectra of solutions of 3-bromopyridine

In the spectrum due to the solution in 3-methyl pentane a broad band extending from 35327 cm^{-1} to 35806 cm^{-1} with the peak at 35650 cm^{-1} was observed which probably corresponds to the $n \rightarrow \pi^*$ transition. The structure was, however, not resolved. The result is in agreement with that reported by Roy (1958) who observed the $n \rightarrow \pi^*$ transition in solution of pyridine in 3-methyl pentane and it was found to be absent in the solution in isobutyl alcohol. This absence of $n \rightarrow \pi^*$ transition in solution in alcohol was explained by Stephenson (1954) and Roy (1958) by assuming that in the solution in alcohol, the non-bonding sp^2 electrons of the nitrogen atom become involved in formation of a hydrogen bond while in the solution in 3-methyl pentane no such bond-formation takes place.

(c) *Spectra in the solid and liquid states*

Both in the liquid and solid states (Fig. 3a and 3b) only one system of broad bands corresponding to the $\pi \rightarrow \pi^*$ transition is produced by this substance and the system due to $n \rightarrow \pi^*$ transition did not appear even when a thick film was used as the absorber

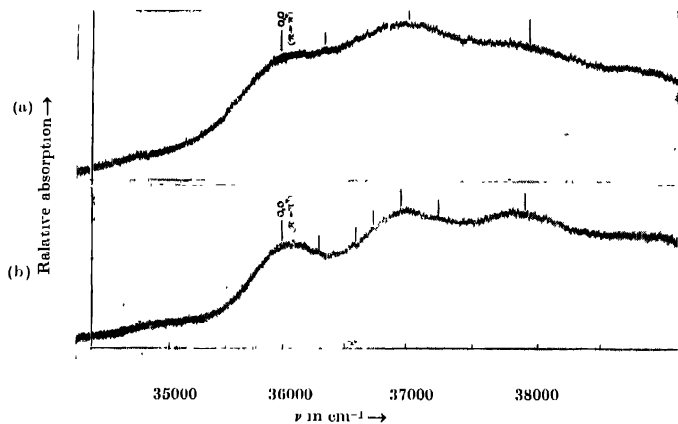


Fig. 3. Microphotometric records of the ultraviolet absorption spectra of 3-bromopyridine

(a) Liquid at 32°C.

(b) Solid at -180°C.

TABLE II

Ultraviolet absorption bands of 3-bromopyridine

Liquid at 32°C		Solid at -180°C		Solution at 32°C	
Wave No. (cm ⁻¹) and intensity	Assign-ment	Wave No. (cm ⁻¹) and intensity	Assign-ment	Wave No. (cm ⁻¹) and intensity	Assign-ment
Transition I		Absent		.08% sol. in alcohol	.08% sol. in 3-methyl pentane
		Absent		Absent	Broad band extended from 35327 cm ⁻¹ to 35806 cm ⁻¹
Transition II	35973 (s) 0, 0	35986 (s) 0, 0		.01% sol in alcohol	
		36268 (w) 0+282		36197 (s) 0, 0	
	36329 (m) 0+356	36570 (mw) 0+584			
		36713 (m) 0+727			
	36943 (s) 0+970	36951 (s) 0+965	37163 (s) 0+966		
		37247 (m) 0+1261			
	37913 (s) 0+2×970	37920 (ms) 0+2×965	38134 (s) 0+2×966		

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In the spectrum due to the liquid the 0,0 band has been identified with that at 35973 cm^{-1} and the other bands indicate a progression of vibrational frequencies 356 and 970 cm^{-1} in the excited state. The 0,0 band of this system thus shifts by about 327 cm^{-1} towards red with the change from the vapour to the liquid state.

When the liquid is solidified and cooled to -180°C , the bands become sharper and assuming the 0,0 band to be at 35986 cm^{-1} , the spectrum can be analysed into a progression of the excited state frequencies 282 , 584 , 726 , 965 and 1261 cm^{-1} . With the solidification of the liquid and lowering of temperature to -180°C , the 0,0 band does not show any further appreciable shift. It is thus evident that the major shift in the position of the 0,0 band occurs when the change of vapour to liquid state takes place.

Similar disappearance of bands due to $n \rightarrow \pi^*$ transition in the liquid and solid states was observed in the case of pyridine and the isomeric picolines (Banerjee, 1956 and 1957). This was explained by assuming that in the condensed phases, the molecules of these compounds form associated groups through the nitrogen non-bonding electron and hydrogen atom of the neighbouring molecules. The results observed in the case of 3-bromopyridine also seem to corroborate the view mentioned above and indicate a similar association of molecules in the liquid and solid states.

It can be seen from Table II that a single excited state frequency 970 cm^{-1} occurs in the case of the liquid and 965 cm^{-1} in the case of the solid state in place of two such frequencies 946 cm^{-1} and 1016 cm^{-1} observed in the spectrum due to the vapour. This is evidently due to broadening of the bands in the former cases caused by the intermolecular field and to consequent overlapping which gives a mean frequency.

2-bromopyridine

(a) Spectrum in the vapour phase

The spectrum due to the 2-bromopyridine in the vapour state yields only one system of discrete bands in the region 37000 cm^{-1} to 39000 cm^{-1} , as can be seen from Figs. 4a and 4b. With the increase in the length of the absorbing path and in the pressure of the absorbing vapour, unlike in the case of 3-bromo isomer, no sharp, narrow and line-like bands due to $n \rightarrow \pi^*$ transition were observed in this case. The weak continuous absorption extending up to about 900 cm^{-1} on the long wavelength side of the 0,0 band due to the $\pi \rightarrow \pi^*$ transition at higher temperature and pressure observed in this case may be due to $v \rightarrow 0$ transition coupled to the electronic transition in $\pi \rightarrow \pi^*$ system. Thus the $n \rightarrow \pi^*$ system is absent in this case. These results thus agree with those reported by Stephenson (1954).

(i) $\pi \rightarrow \pi^*$ transition (Transition II)

The strong band at 36958 cm^{-1} has been taken to be the 0,0 band and the analysis of the other bands has yielded the excited state vibrational frequencies 136, 280, 653, 742, 954, 1053 and 1554 cm^{-1} as shown in Table III.

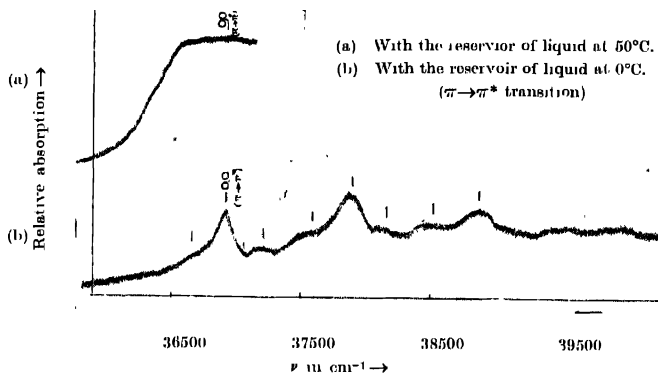


Fig. 4 Microphotometric records of ultraviolet absorption spectra of 2-bromopyridine in the vapour state.

The infrared absorption spectra of a very thin film of 2-bromopyridine was studied with rocksalt optics in order to find out the ground state vibrational frequencies. The wave numbers of the observed infrared bands are 698 (ms), 756 (s), 988(ms), 1040(w), 1075(s), 1103(s), 1148(vw), 1282(vw), 1418(s), 1451(ms) and 1563(s), the strengths of absorption being given in the parentheses.

The upper state vibrational frequencies 653, 742 and 954 cm^{-1} can be correlated to the ground state frequencies 698, 756 and 988 cm^{-1} observed in the infrared absorption. The vibrational frequencies 1053 cm^{-1} and 1554 cm^{-1} in the excited state probably correspond to the infrared frequencies 1075 cm^{-1} and 1563 cm^{-1} respectively.

As regards the band at a distance of 280 cm^{-1} on the shorter wavelength side of the 0,0 band, a band at 292 cm^{-1} on the longer wavelength side has been recorded. This band which probably represents the ground state frequency has not been observed in the infrared absorption because of limitation of NaCl optics used. The band at 136 cm^{-1} on the shorter wavelength side of the 0,0 band might represent a $0 \rightarrow v'$ transition. The assignment is not improbable for such low frequency transition is observed in the case of 3-bromo isomer and other substituted pyridine compounds (Rush and Sponer, 1952).

TABLE III

Ultraviolet absorption bands of 2-bromopyridine in the vapour state

Wave No. (cm ⁻¹) and intensity	Assignment	Wave No. (cm ⁻¹) and intensity	Assignment
Transition I		Transition II	
Absent		36006 (w)	0-292
		36958 (s)	0, 0
		37094 (w)	0 136
		37238 (m)	0 280
		37611 (m)	0 653
		37700 (w)	0-1742
		37912 (s)	0 954
		38011 (vw)	0 1053
		38178 (m)	0 1220
			0 280 954
		38512 (ms)	0 1554
		38870 (s)	0 2-954

A comparison of the absorption spectra of 2-bromopyridine and pyridine in the vapour state shows that the 0,0 band of 2-bromopyridine is shifted by about 1392 cm⁻¹ towards red with respect to that of the latter compound. A similar substitution by CH₃ group in α -picoline shifts the 0,0 band only by 730 cm⁻¹.

(b) *Spectra of solutions*

When 2-bromopyridine is dissolved in alcohol, at a concentration of .01% by weight and a path length of 5 mm, the band system due to $\pi \rightarrow \pi^*$ transition appears with the 0,0 band at 36753 cm⁻¹ and the other bands are represented by progression of frequencies 971 cm⁻¹ and 655 cm⁻¹ in the excited state (Fig. 5c). It can be seen that in the case of .01% solution in alcohol the 0,0 band is shifted by about 200 cm⁻¹ towards long wavelengths from the 0,0 band due to the vapour.

On gradually increasing the concentration of the solution from .01% to .08% by weight, a continuous absorption due to $v \rightarrow 0$ transition of $\pi \rightarrow \pi^*$ system is observed in the region 35500 cm⁻¹ to 36700 cm⁻¹ as is evident from the absorption curve reproduced in Fig. 5. A similar absorption is also observed in case of .08% solution in 3-methyl pentane, but no band system due to $n \rightarrow \pi^*$ transition as observed in the case of 3-bromopyridine could be detected in this case.

This is an agreement with the conclusions of Stephenson (1954) who earlier studied the absorption spectra of solution of 2-bromopyridine in alcohol and in iso-octane and from the similarity of the two absorption curves concluded that the $n \rightarrow \pi^*$ transition is absent in the spectrum due to the 2-bromopyridine molecule.

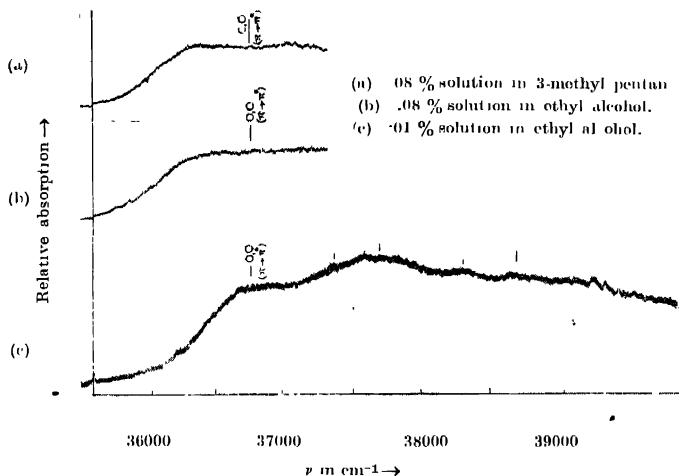


Fig 5. Microphotometric records of the ultraviolet absorption spectra of solutions of 2-bromopyridine.

(c) Spectrum in the liquid and solid states

In the spectrum of 2-bromopyridine in the liquid state only one system of discrete bands consisting of three broad bands due to Transition II is observed (Fig. 6), the band at 36571 cm^{-1} being taken as the 0,0 band of this system. Thus the 0,0 band shifts by about 387 cm^{-1} towards longer wavelengths with liquefaction of the vapour. The other bands can be assigned to a progression of the excited state frequency 918 cm^{-1} . When the liquid is frozen and cooled to about -180°C , these bands become a little sharper, but the bands are not resolved into sharper components. The shift of the bands with liquefaction of the vapour is much larger than that observed in spectrum due to the solution in alcohol. The 0,0 band in this case is at 36479 cm^{-1} and the other two bands are assigned to a progression of the upper state vibrational frequency 971 cm^{-1} . Thus with

solidification and cooling the substance to about -180°C , the 0,0 band undergoes a small shift of 92 cm^{-1} towards red.

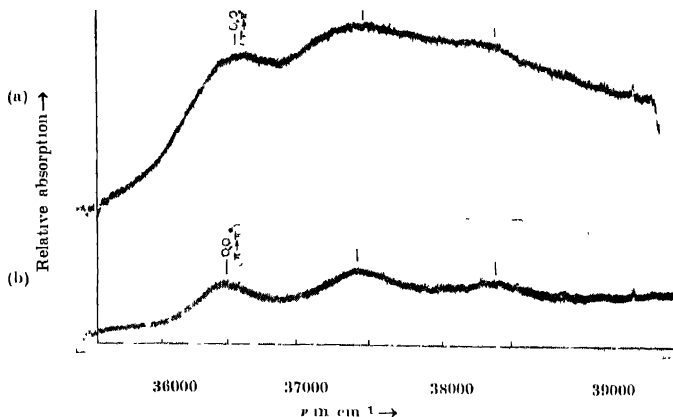


Fig. 6. Microphotometric records of the ultraviolet absorption spectra of 2-bromopyridine.

- (a) Liquid at 32°C .
(b) Solid at -180°C .

TABLE IV
Ultraviolet absorption bands of 2-bromopyridine

Liquid at 32°C		Solid at -180°C		Solution at 32°C	
Wave No. (cm $^{-1}$) and intensity	Assignment	Wave No. (cm $^{-1}$) and intensity	Assignment	Wave No. (cm $^{-1}$) and intensity	Assignment
Absent		Absent		Absent	
Transition I		Absent		0.08% sol. in alcohol	0.08% sol. in 3-methyl pentane
				Absent	
				Absent	
				Absent	
Transition II		0.01% sol. in alcohol		36571 (s)	0, 0
				37408 (m)	0+655
				37480 (vs)	0+918
				38379 (s)	0+971+655
38400 (ms)		0+2×918		38697 (s)	
38420 (ms)		0+2×971		0+2×971	

When thicker film of thickness of the order of 10 microns is used, the $\pi \rightarrow \pi^*$ system produces continuous total absorption but no other band system in the low energy region corresponding to $n \rightarrow \pi^*$ transition is produced by the substance either in the liquid state or in the solid state at -180°C .

It is concluded that in the case of 2-bromopyridine the $n \rightarrow \pi^*$ transition is absent whether the substance is in the vapour phase, in solutions or in the states of aggregation. As postulated by Stephenson (1954) this may be due to the inductive attraction of the halogen atom attached to the carbon atom adjacent to the nitrogen atom which increases the binding energy of the non-bonding electron over that existing in pyridine, thereby shifting the $n \rightarrow \pi^*$ transition into the spectral region of $\pi \rightarrow \pi^*$ transition and the situation is not altered when the molecules are in solutions and also in the state of aggregation.

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